PART I
THE POLYMER OF METHYL ISOPROPENYL KETONE

PART II
THE DISSOCIATION OF SUBSTITUTED HEXAARYLETHANES

BY
JOHN WARREN MEIER
B.S., University of Wisconsin, 1938

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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PART I

THE POLYMER OF METHYL ISOPROPENYL KETONE

Introduction

In spite of the industrial importance of the polymers of acrylic and methacrylic acid and their esters, the exact linear structures of the polymers are not known. The polymers of methyl vinyl ketone[1] and methyl isopropenyl ketone[2] have been shown to be of the "head to tail" structural type. The oxidations of these polyketones under the proper conditions would yield, respectively, polyacrylic acid and polymethacrylic acid of "head to tail" structure from which related polymers could be prepared for comparing with existing products. In this manner the structures of the latter could be evaluated.

This investigation was undertaken to attempt the above-mentioned oxidations preliminary to the indicated comparisons. An investigation of the synthesis and polymerization of methyl isopropenyl ketone was also made.

Experimental and Discussion

A study of the action of aqueous sodium hypochlorite on the polymer of methyl vinyl ketone showed that, depending on the conditions, partial or complete destruction of all polymeric matter resulted. None of the desired polyacrylic acid could be obtained.

Methyl isopropenyl ketone was prepared by the condensation of ethyl methyl ketone with formaldehyde in the presence of alkali followed by the dehydration of the resulting 2-methyl-3-ketobutanol-1 by means of anhydrous oxalic acid.[3] This compound was caused to polymerize by the action of heat or ultra-violet irradiation.

The polymer of methyl isopropenyl ketone was found to be much less reactive with aqueous sodium hypochlorite than was that of methyl vinyl ketone. In this case, as above, none of the desired polyacid was obtained.

Attempts to oxidize the polymer of methyl isopropenyl ketone by means of chromic anhydride in glacial acetic acid resulted in a polymer which contained chromium. Attempts to remove the metal resulted in the destruction of all polymeric material.

The destructive distillation of the polymer of methyl isopropenyl ketone under diminished pressure resulted in small amounts of volatile products which were too complex to yield information as to the structure of the polymer.

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PART II

THE DISSOCIATION OF SUBSTITUTED HEXAARYLETHANES

Introduction

Since Gomberg's discovery[1] of the dissociation of hexaphenylethane, numerous attempts have been made to explain this phenomenon. This investigation was undertaken to extend the number of halogen-substituted hexaarylethanes studied in this laboratory[2,3,4] and to obtain additional evidence in regard to the theories concerning the cause of dissociation which have been brought forth as the result of these previous studies.

Experimental and Discussion

The following hexaarylethanes have been prepared in solution and the degrees of dissociation have been measured in 0.1 M. solution at 25° by means of the magnetic susceptibility method[5,6]: di-*m*-tolyltetra-*p*-*tert*-butylphenylethane (42%), di-*o*-tolyltetra-*p*-*tert*-butylphenylethane (82%), di-*m*-bromophenyltetra-*p*-*tert*-butylphenylethane (40%), di-*o*-bromophenyltetra-*p*-*tert*-butylphenylethane (66%), di-*m*-tolyltetra-*p*-tolylethane (2%), diphenyltetra-*p*-fluorophenylethane

(5.3%), hexa-*p*-fluorophenylethane (3.8%), tetraphenyldi-*m*-fluorophenylethane (5.8%), diphenyltetra-*m*-fluorophenylethane (3.9%).

The ethanes containing four *p-tert*-butyl groups and two *ortho* or *meta* bromo or methyl groups were found to dissociate to a much larger extent than that predicted on the basis of the weight, symmetry and steric effects.[2,3,4] The low dissociation of di-*m*-tolyltetra-*p*-tolylethane shows that the high values are not due only to the positions of the groups.

The fluorine-substituted ethanes were found to dissociate in accordance with expectations except for hexa-*p*-fluorophenylethane and diphenyltetra-*m*-fluorophenylethane, the values for which were low. The known lability of *para* halogens in this type of compound[7] may account for the low value in the case of the former.

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VITA

The writer was born in Madison, Wisconsin on January 26, 1916. He attended the elementary schools of that city and graduated from Madison Central High School in June, 1934. In September of that year he entered the University of Wisconsin where he was granted the degree of Bachelor of Science in June, 1938. Since September, 1938 he has been studying for the degree of Doctor of Philosophy in Chemistry at the University of Illinois where he has held assistantships in chemistry during the school years 1938-1939, 1939-1940 and 1941-1942. During the school year 1940-1941 he was a National Defense Research Assistant.

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